

Molecular design and synthesis of heterogeneous and single-site, supported catalysts

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Abstract

This contribution describes a non-aqueous, molecular precursor approach to the preparation of mixed-element oxides, which allows a degree of molecular-level control over the nanostructure of the resulting materials. This approach, referred to as the *thermolytic molecular precursor* method, has been used to obtain highly dispersed mixed-element oxide materials. In some cases, this methodology provides heterogeneous catalysts which possess superior properties relative to catalysts with the same composition, but prepared by traditional aqueous methods. It has also been found that certain molecular precursors are useful for introduction of surface-bound catalytic species. With this method, multicomponent molecular precursors may be used to produce porous materials with nano-sized voids. This affords mixed-oxide materials with a homogeneous dispersion of metal atoms throughout the inorganic framework walls of a mesoporous material. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Molecular precursor; Catalysis; Heterogeneous; Single-site; Selective oxidation

1. Introduction

Advances in catalysis will continue to play an important role in the world economy, improving the quality of the environment, and allowing for more efficient use of energy resources [1–3]. This progress, which will encompass improvements in the performance of currently employed catalysts and developments of new catalytic processes, can be dramatically accelerated by fundamental research on structure–reactivity relationships that govern catalyst activity and selectivity. Investigations of these mechanistic issues will be particularly challenging in

heterogeneous catalysis, for which the active sites are difficult to characterize under reaction conditions.

As in the past, significant progress in catalysis research will require development of methods for the synthesis of specific, complex solid state structures. Heterogeneous catalysts represent difficult targets, since synthetic control over the detailed structures of complex solids is still at a rather primitive stage of development. Despite many recent breakthroughs in methodologies for solid state synthesis, there are few general principles that can be used in the preparation of complex structures (especially metastable ones) that will perform a specific function as a catalyst. Thus, the development of such generally useful synthetic principles remains a central theme in catalysis research. The ability to synthesize specific structures, in which atoms are arranged in a predetermined way, should lead to rapid assessments of theories

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on structure–property correlations, and of course to efficient assembly of the best “candidate structures”.

The properties of a catalyst are known to be sensitive to several structural features operating on both the atomic and nanostructural scales, and these should be brought under synthetic control. At the atomic level, the spatial arrangement of metal atoms on a catalyst surface plays a crucial role in the activation of substrates. For active sites involving more than one kind of metal atom (e.g., in bimetallic catalysts), the synthesis of heteroatomic linkages is of great importance. For example, the M–O–M' heterolinkages in bimetallic oxides, or at catalyst–support interfaces, are associated with novel chemistry and in some cases high Brønsted acidities [4–10]. Many important catalytic properties are derived from nanoscaled structural features. Thus, synthetic control over nanostructure is essential to the optimization of catalyst performance, in several ways. Specific chemical properties associated with nanoscaled features include supported monolayers, dispersed catalytic nanoparticles, catalyst–support interfaces, and framework mesoporosity.

Recent years have witnessed notable progress in the development of synthetic routes to solid state materials [11,12]. Considerable effort has been devoted to the use of sol–gel routes in the synthesis of multicomponent oxide materials, and this methodology has proven relatively successful in the production of homogeneous systems [13–16]. The use of “single source” molecular precursors has gained considerable popularity, as this approach offers great potential for providing designed solid state structures with properties tailored at the molecular level [17–22]. However, this approach has been employed mostly in the synthesis of electronic materials. In related endeavors, much progress is being made in the development of methods for producing nanoparticles with controlled sizes, shapes, and compositions [23–27]. New synthetic methods also target organic or inorganic supramolecular materials, which have components organized into complex structures with tailored properties [28,29]. Some structures of the latter type, which feature both organic and inorganic components, have been referred to as hybrid organic/inorganic materials. In general, these hybrid materials offer considerable potential for the construction of materials with novel properties. Recent years have seen important advances in the ability to produce, via templating methods, materials with

framework porosity [30,31]. Thus, pores that cover a wide range of dimensions are now accessible, but it is still difficult to synthetically control the shapes of pores in a solid.

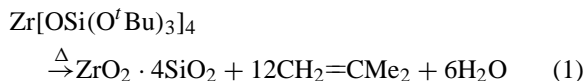
Breakthroughs in materials chemistry are often brought about by the serendipitous discovery of new synthetic pathways. Furthermore, many important synthetic methods that are used to produce intricate architectures, such as those used for zeolitic materials, remain poorly understood. Future efforts should strive to develop general methods for the precise synthesis of predetermined structures. New, advanced materials will undoubtedly result from chemically directed, low-temperature synthetic routes that operate at the molecular or atomic level. Creative methods for materials synthesis will allow a broader effort in targeting compositions and structures that could represent new generations of catalysts. For example, it should be possible to employ organic/inorganic hybrids and molecular precursors to tailor the precise structure of a catalyst's active site. An approach with considerable potential for producing novel active sites involves chemical transformations on the derivatized surface of a support material. This approach, which includes what can be described as “surface organometallic chemistry” has been used by the Basset group in Lyon to prepare highly active catalysts for hydrocarbon cracking [32]. Methodologies that employ templates for the introduction of porosity may be refined and tailored to allow great diversity in applications to substrate-specific, shape-selective catalysis. In addition, new developments in synthesis will allow better control over the size, shape and composition of catalytic nanoparticles.

Our program in the synthesis of heterogeneous catalysts focuses on strategies that feature molecular design and synthesis. The fundamental approach is based on use of molecular chemistry in the low-temperature construction of solid-state networks. As discussed below, one strategy focuses on use of oxygen-rich, “single-source” molecular precursors that cleanly convert to mixed-element oxide materials possessing properties derived from the molecular origin of the solid-state building blocks [33–45]. A second approach involves use of dendrimeric macromolecules with chemically functionalized surfaces as nanostructured building blocks for the synthesis of higher-order materials and porous networks [46–48].

2. Results and discussion

2.1. Thermolytic molecular precursor route to solid state materials

Studies over the past decade have shown that transition-metal and main-group element complexes of $\text{OSi}(\text{O}^t\text{Bu})_3$ and $\text{O}_2\text{P}(\text{O}^t\text{Bu})_2$ ligands are convenient precursors to homogeneous (well-dispersed), metal oxide–silica, metal silicate, and metal phosphate materials [33–45]. In this approach, the targeted oxide-based materials are derived from tailored, oxygen-rich precursor molecules. These precursors have been found to readily transform via elimination of isobutylene and water at remarkably low temperatures (100–200 °C) to form $\text{M}_x\text{Si}_y\text{O}_z$ or $\text{M}_x\text{P}_y\text{O}_z$ materials. For example, $\text{M}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$ ($\text{M} = \text{Zr}, \text{Hf}$) complexes smoothly decompose quantitatively upon gentle heating (100–140 °C) to homogeneous $\text{MO}_2 \cdot 4\text{SiO}_2$ materials in the solid state or in solution (Eq. (1), [37]), cleanly producing isobutylene and water as the only byproducts. Decomposition of $\text{Zr}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$ in refluxing toluene, xylene or mesitylene gives a transparent gel, which has a high surface area of $520 \text{ m}^2 \text{ g}^{-1}$ and has been shown by electron microscopy to be composed of 30–70 nm diameter particles.



This thermolytic molecular precursor method offers a number of advantages over the widely employed sol–gel route. A general goal of our work in this area

is to establish correlations between the chemical properties of molecular precursor building blocks and the catalytic properties of the new materials derived therefrom. Such correlations might form the basis for new design principles for the synthesis of useful heterogeneous catalysts. For example, it was shown that this molecular approach can provide homogeneously dispersed metal sites in a silica support matrix [37,41,44]. This is relevant in that it is often the case that highly homogeneous systems ($\text{ZrO}_2\text{--SiO}_2$, $\text{TiO}_2\text{--SiO}_2$, etc.) exhibit superior catalytic activities [4–10].

The construction of nanostructured materials with tailored properties is a challenging goal that is widely regarded as representing a key first step toward new technologies. Recent work with poly(alkylene oxide) block copolymer templates as structure-directing agents has shown that the thermolytic molecular precursor method represents an exciting new approach to a wide range of materials with complex compositions and mesoporosities [49,50]. Based on use of molecular precursors in the presence of block copolymer templates, mesoporous, multicomponent oxides (denoted UCB1) have been prepared. This method has been demonstrated for materials with the compositions $\text{ZrO}_2 \cdot 4\text{SiO}_2$, $\text{Ta}_2\text{O}_5 \cdot 6\text{SiO}_2$, $\text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$, and AlPO_4 (Table 1). The new materials are mesoporous mixed-element oxides with high surface areas, homogenous dispersions of elements and thick framework walls. The templating mechanism by which the UCB1 materials form is quite interesting, since it occurs under non-aqueous conditions, and in non-polar solvents. Previous reports on template-assisted mesoporous metal oxide formation describe synthetic

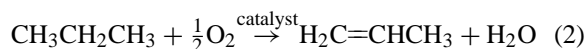
Table 1
Data for the UCB1 materials

Oxide	Precursor	Template	UCB number	Surface area (m^2/g)	Pore radius (Å)	d_{100} (Å)	Wall thick (Å)
$\text{ZrO}_2 \cdot 4\text{SiO}_2$	$\text{Zr}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$	$\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$	UCB1-ZrSi	540	22	110	66
$\text{ZrO}_2 \cdot 4\text{SiO}_2$	$\text{Zr}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$	$\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$	UCB1-ZrSi	545	20	111	71
$\text{ZrO}_2 \cdot 4\text{SiO}_2$	$\text{Zr}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$	$\text{EO}_{20}\text{PO}_{30}\text{EO}_{20}$	UCB1-ZrSi	490	13	110	84
$\text{ZrO}_2 \cdot 4\text{SiO}_2$	$\text{Zr}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$	$\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$	UCB1-ZrSi	560	13	100	74
$\text{ZrO}_2 \cdot 4\text{SiO}_2$	$\text{Zr}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$	$\text{H}_{33}\text{C}_{16}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$	UCB1-ZrSi	530	16	113	81
$\text{Ta}_2\text{O}_5 \cdot 6\text{SiO}_2$	$(\text{EtO})_2\text{Ta}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$	$\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$	UCB1-TaSi	400	19	106	68
$\text{Ta}_2\text{O}_5 \cdot 6\text{SiO}_2$	$(\text{EtO})_2\text{Ta}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$	$\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$	UCB1-TaSi	440	19	110	72
AlPO_4	$(\text{PriO})_2\text{AlO}_2\text{P}(\text{O}^t\text{Bu})_2$	$\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$	UCB1-AlP	670	39	111	33
AlPO_4	$(\text{PriO})_2\text{AlO}_2\text{P}(\text{O}^t\text{Bu})_2$	$\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$	UCB1-AlP	750	33	113	47
$\text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$	$\text{Fe}[\text{OSi}(\text{O}^t\text{Bu})_3]_3 \cdot \text{THF}$	$\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$	UCB1-FeSi	400	12	102	80
$\text{Fe}_2\text{O}_3 \cdot 6\text{SiO}_2$	$\text{Fe}[\text{OSi}(\text{O}^t\text{Bu})_3]_3 \cdot \text{THF}$	$\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$	UCB1-FeSi	355	17	105	71

protocols that employ highly polar (usually aqueous) reaction solvents. Very little is known concerning the phase behavior of poly(alkylene oxide) block copolymers in non-aqueous solvents; however, the observation concerning formation of the mesostructured UCB1 materials in a non-polar environment would seem to have important implications for the synthesis of nanostructured materials. It is anticipated that this new molecular precursor route will allow access to a wide range of materials with more complex compositions and intricate nanoarchitectures, and these structures may be useful in catalysis.

2.2. Thermolytic molecular precursor route to catalysts for the oxidative dehydrogenation of propane

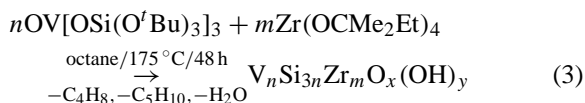
An important challenge in chemistry is the design and development of new catalysts for selective transformations of saturated hydrocarbons [51–53]. For example, the high demand for alkenes has motivated interest in their production from inexpensive, light alkanes. The dehydrogenation of light alkanes proceeds only at high temperatures, where cracking and the deposition of carbon present serious problems. On the other hand, oxidative dehydrogenation (ODH) is thermodynamically favored at lower temperatures and does not suffer from coking, which decreases catalyst performance [51]. Thus, the ODH of propane Eq. (2) is of interest as an alternative source of propene, especially given its high demand for the production of polypropylene, acrylonitrile, and propene oxide [54]. However this selective oxidation is particularly challenging, given the high reactivity of propene toward further oxidation [51,55].



In the development of a molecular precursor route to ODH catalysts, an important discovery was that the composition of materials derived from the thermolytic molecular precursor route may be greatly expanded by cothermolyses in solution [38,42]. Often, it is observed that such thermolyses give well-dispersed materials. Interestingly, the molecular mixtures typically decompose at temperatures lower than the decomposition temperature of the pure components. Apparently, the polymerizing species in solution can randomly

incorporate the building blocks of both precursors into the developing network, with little selectivity. This method is inherently versatile, allows control over elemental composition, and should be applicable to many catalyst formulations. Initially, this approach was investigated in the synthesis of catalysts for the ODH of propane.

Utilizing $\text{OV}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$ and $\text{Zr}[\text{OCMe}_2\text{Et}]_4$, a series of catalysts with varying vanadium content (2–33 wt.%) were prepared and these were compared to catalysts of similar stoichiometry that were prepared by conventional (impregnation) methods (Eq. (3)). The surface areas of the catalysts prepared from molecular precursors were very high (up to $466 \text{ m}^2 \text{ g}^{-1}$ after calcination at 773 K) and selectivities for propene were as high as 95.5 at 0% conversion and 673 K. Characterization of these catalysts showed that the more active compositions (10–18% vanadia) appear to contain oligomeric tetrahedral vanadium sites. The V/Si/Zr/O catalysts with 18 and 23% V_2O_5 compared favorably to the most selective and active catalysts reported for propane ODH, and exhibited catalytic properties that were superior to those of previously reported vanadium-based catalysts. Most significantly, the novel features and impressive performance for these materials suggested that molecular-level control over structure can provide new generations of superior catalysts [38].



Molecular precursors have also been used to prepare zirconia-dispersed vanadia catalysts. Low-temperature cothermolysis of $\text{OV}(\text{O}^t\text{Bu})_3$ and $\text{Zr}(\text{OCMe}_2\text{Et})_4$ in a non-polar solvent were used to produce amorphous V/Zr/O oxides in which the V and Zr were thoroughly dispersed throughout the oxide matrix. Following calcination at elevated temperatures, nanocrystalline zirconia and various VO_x species supported on the surface of the zirconia crystallites appeared. In general, the VO_x/ZrO_2 materials prepared from molecular precursors possess a higher surface area and dispersion of VO_x species than materials of the same composition prepared by conventional impregnation methods. For the catalysts derived from alkoxides, the maximum rate for propane ODH is more than double

that observed for VO_x/ZrO_2 materials prepared by impregnation. In addition, the materials derived from molecular precursors exhibit enhanced selectivities toward the ODH (versus combustion) of propane [42].

Since the thermolytic molecular precursor method involves non-aqueous conditions, V_2O_5 does not form readily during calcination. In this method, it seems that the nucleation and growth of VO_x species on the zirconia surface occurs in a more controlled manner, under conditions that do not favor agglomeration of the vanadia into V_2O_5 particles, to give materials that have a greater dispersion of VO_x on zirconia. This is supported by the observation that polyvanadate structures exhibit higher specific activity and selectivity for propene formation [56–58]. The VO_x/ZrO_2 catalysts as produced upon thermolysis contain intimately mixed vanadium and zirconium oxides. Upon calcination, the zirconia segregates into a nanocrystalline phase, and vanadia spreads efficiently as VO_x species onto the surface of the nucleated zirconia.

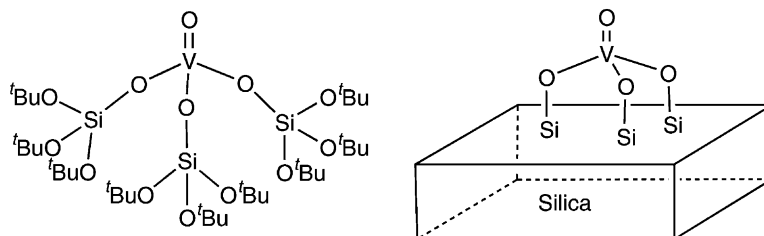
2.3. Molecular precursor routes to single-site catalysts

Like many of the molecular precursors under investigation in our laboratories, the vanadium complex $\text{OV}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$ also serves as a useful model for isolated sites on the surface of a support (Scheme 1). As multiple spectroscopic techniques have shown, the vanadium in $\text{OV}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$ adopts an environment that is very similar to that exhibited by highly dispersed vanadium on a silica support. For example, the ^{29}Si NMR shift of this model complex is extremely similar to those observed for porous vanadium silicates. Utilizing Raman and infrared spectroscopies, it was possible to characterize the V–O, V=O and Si–O–V vibrations. These assignments have

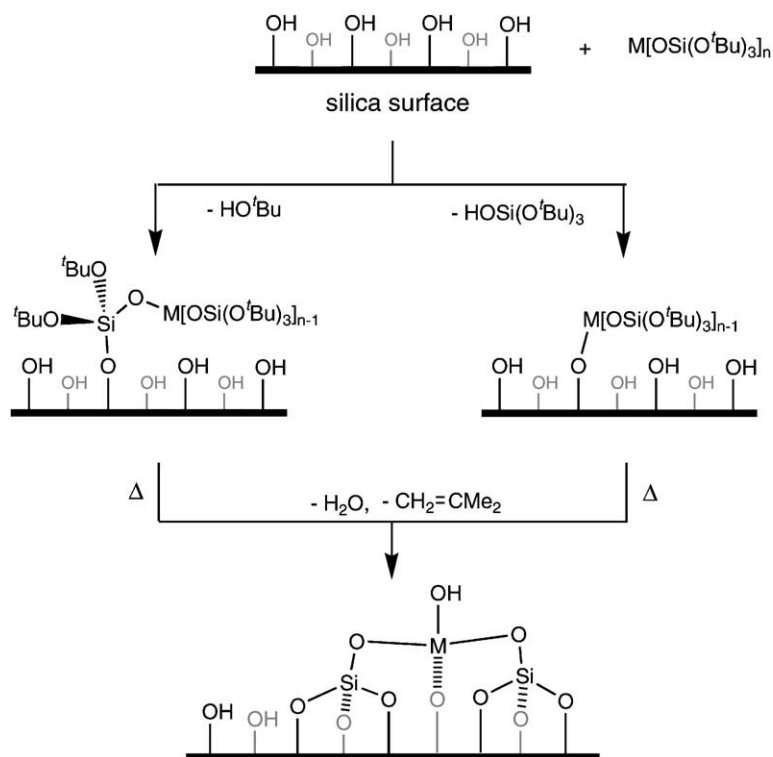
led to insights into the structural characterization of single-site vanadium catalysts [40].

The thermolytic molecular precursor route to oxide materials may be used to introduce catalytic sites onto the surface of an oxide support. Potential advantages to this approach derive from the molecular-level control that may be exerted over the structure of the catalytic site. This general method is illustrated by the postulated transformations shown in Scheme 2. First, the precursor is bonded to the surface of the oxide support (e.g., silica) via protonolysis reactions. For the case of an alkoxy(siloxy) species of the type $\text{M}[\text{OSi}(\text{O}^t\text{Bu})_3]_n$, this surface-attachment chemistry may occur with loss of HO^tBu or $\text{HOSi}(\text{O}^t\text{Bu})_3$, to result in bonding to the surface through M–O–(surface) or Si–O–(surface) linkages, respectively. Calcination should then lead to introduction of $\text{MO}_x \cdot n\text{SiO}_2$ or $\text{MO}_x \cdot (n-1)\text{SiO}_2$ species onto the oxide surface, in a manner similar to that observed for bulk transformations. Thus, the new site may be “partially supported” by the few equivalents of silica that are derived from the molecular precursor. This latter effect is expected to aid in the introduction and stabilization of single metal atom sites.

The method outlined above was first investigated for the introduction of titanium sites onto silica. Titania–silica materials have attracted considerable recent attention due to their performance as selective oxidation catalysts. For example in the 1970s, Shell developed a silica-supported titania epoxidation catalyst for the production of propylene oxide [59–61]. Many other titania–silica materials have been studied in this context, including the titanium-substituted molecular sieves TS1 and TS2 [62–65], the titanium substituted zeolite Ti- β [66], and Ti-MCM41 (where the titanium is incorporated into the walls of the mesoporous host [67,68] or grafted onto its



Scheme 1.



Scheme 2.

surface [69]). Our work initially focused on use of the precursor $\text{Ti}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$, which is known to be an efficient source of dispersed $\text{TiO}_2 \cdot 4\text{SiO}_2$ materials [41].

Treatment of aerosil silica samples with the titanium precursor provided catalysts which proved to be highly active in the selective oxidation of cyclohexene to cyclohexene oxide, using cumene hydroperoxide as the oxidant. Calcination of this material led to a catalyst that was less active, but still more active than the Shell catalyst derived from treatment of silica with $\text{Ti}(\text{O}^i\text{Pr})_4$. Thus, in both the calcined and uncalcined material, the $-\text{OSi}(\text{O}^t\text{Bu})_3$ ligand appears to provide a beneficial effect on the structure of the supported catalytic site. In particular, the trialkoxy(siloxy) ligand set probably serves to produce isolated $-\text{O}-\text{Ti}(-\text{O}-\text{Si})_3$ sites on the catalyst surface.

Given the promising results observed for this titanium system, we explored the synthesis of other single-site catalysts prepared from oxygen-rich

titanium precursors. For the molecular precursors, the Ti:Si ratio was varied to probe the influence of siloxy ligands on the grafting chemistry and the catalytic behavior of the resulting catalysts. These comparisons showed that fewer siloxide ligands typically result in greater titanium loadings. This is attributed to the steric properties of the $-\text{OSi}(\text{O}^t\text{Bu})_3$ ligand, which can retard the protonolysis reaction in the more sterically encumbered cases (i.e., $\text{Ti}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$). On the other hand, the siloxy ligands provide an enhancement of the catalytic activity and selectivity [70]. Thus, the optimum precursor was found to be the tris(siloxide) (^iPrO) $\text{Ti}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$ [71]. The support materials investigated in these cases were aerosil and the high surface-area, mesoporous silicas MCM-41 [72] and SBA-15 [73]. The best results, in terms of catalyst performance, were observed for the tris(siloxide) as precursor and a mesoporous silica as support. The results obtained for MCM-41 and SBA-15 were very similar.

3. Conclusion

The thermolytic molecular precursor route to heterogeneous catalysts can provide a number of advantages. These include the production of high surface areas and high dispersions of elements within an oxide material. In addition, we have observed certain benefits that seem to relate to the molecular chemistry involved in network formation. In some cases, it has been found that this approach leads to nanostructures which do not resemble the molecular species from which they are derived. However, these structures have catalytic properties that are distinctly better than similar structures obtained by conventional, aqueous methods. We attribute these results to a more highly dispersed material that is initially generated by the thermolytic molecular precursor method. This can result in a more complete conversion to catalytically active material, relative to more traditional routes based on aqueous impregnation methods. In the case of vanadium-containing catalysts, the use of non-polar solvents suppresses the tendency of vanadia to agglomerate into V_2O_5 domains. Finally, modifications of the molecular precursor method allow the production of single site catalysts, for which structural and catalytic properties may be synthetically manipulated.

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